

Atomistic Simulation of Polymer Adhesion

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〈概要〉

金属とポリマーの密着性は、様々な技術製品にとって重要である。密着性を調査するために、銅とポリイミドの界面における原子レベルの手法を使った計算機シミュレーションのフレームワークを開発した。本アプローチでは、剥離過程におけるナノメートルスケールのシミュレーションに力場分子動力学が、さらにパラメータの検証とパラメータの調整に密度汎関数理論が使われている。

様々な剥離速度条件下で、ポリマーを金属面から剥がす際の剥離力とエネルギーの計算がおこなわれた。本シミュレーションにより、界面強度の定性的な予測や、原子レベルでの過程についてより良い理解を得ることができる。さらに、異なる材料の組み合わせから成る同様な構成への適用が可能である。

1. INTRODUCTION

Adhesion, the attractive force experienced at the interface of dissimilar materials, plays an important role in the performance of various technological materials. Adhesion strength defines how easily the contact surfaces can be separated by mechanical deformation. Understanding and controlling adhesion is required in material processing. An example is the polymer-metal interfaces which are present in insulated cables and semiconductor products (Figure 1). Here we report on the development of simulation methods to evaluate adhesion of polyimide, pyromellitic dianhydride-oxydianiline (PMDA-ODA) and copper, Cu.

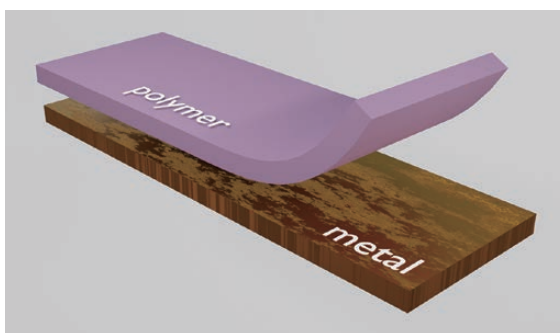


Figure 1 Conceptual schematic figure of the polymer-metal interface and peeling.

Adhesive properties of interfaces typically are evaluated experimentally, for example, by peel test measurements. From the theoretical point of view adhesion phenomena

are described by various theories of adhesion rather than by a single concept. For example, in one case the relevant mechanism is the mechanical interlock operating at micro-level, while in other cases the formation of chemical bonds formed in the range of few atomic distances that determines adhesive properties.

In computational approaches, adhesion can be investigated at various physical length-scales. Here we report on a materials simulation study of polyimide-copper (PI-Cu) using a nano-scale atomistic dynamical model that contains up-to 100.000 atoms and simulation time in the order of 1 ns. In our simulation framework, the force-field MD method was used to compute adhesion setups. For validation and parameter fitting, the DFT computations were performed on small-sized model configurations. For examples of similar simulation studies for adhesion, see REFERENCES^{1), 2)}. Our goal was to combine various computational methods and tools for a simulation framework shown in Figure 2. In the next section, the elements of the simulation model, the force-field, the initial geometry generation, and the loading are discussed in detail.

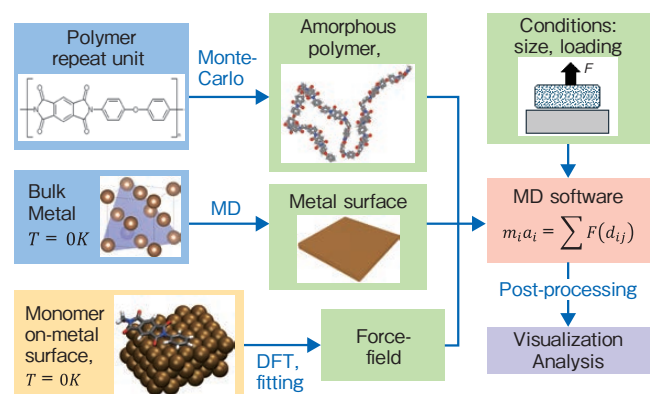


Figure 2 An overview of the simulation framework and components for adhesion computation.

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2. COMPUTER SIMULATION METHOD

Computational materials science aims to understand and predict the structure and properties of technological materials. Our primary approach is the atomic-level, classical Molecular Dynamics method. In the force-field approach, the dynamics of the system are described by classical mechanical equations of motion. The energy of the system is computed by interatomic potential functions and the micro- and macro-scopic properties are derived from the time-evolution of the system. The functional form and parameters of the interatomic potential depends on the material type and applications. We used Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), general-purpose MD software³⁾.

In case of polyimide, we used the Optimized Potentials for Liquid Simulations (OPLS), all-atom, molecular mechanics, force-field⁴⁾. The total energy of atomic system is computed as a sum of bonded and non-bonded terms, $E_{total} = E^B + E^{NB}$, in the following energy terms,

$$E^B = \sum_{bonds} K_r (r - r_0)^2 + \sum_{angles} k (\theta - \theta_0)^2 + \sum_{dihedrals} \frac{V_1}{2} (1 + \cos \phi) + \frac{V_2}{2} (1 - \cos 2\phi) + \frac{V_3}{2} (1 + \cos 3\phi)$$

$$E^{NB} = \sum_{ij} \frac{q_i q_j}{r^2} + \sum_{ij} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

The inter-atomic distance is r , bond angle is θ and the dihedral angle is ϕ . The bond stretch energy is parameterized by K_r, r_0 , the bond angle term by k, θ_0 and the dihedral angle term by V_i . The modes of molecule deformations, such as bond stretch, bending and torsion are represented by the energy terms: bond, angle and dihedral as illustrated in Figure 3.

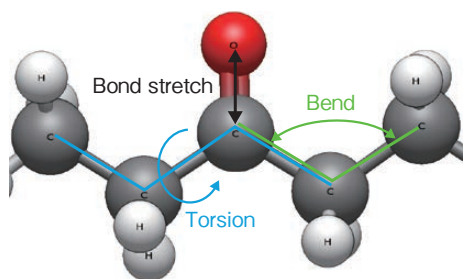


Figure 3 The bonded interaction terms are explained in the case of a model polymer segment.

The non-bonded terms include the electrostatic interaction of atomic partial charges, q_i , due to polarization and the Lennard-Jones 12-6 potential, see Figure 4, describing the dispersive interaction. While this type of force-field is typical in bio-materials simulations it can be naturally extended to systems of polymers and organic solvents. The chemical bond topology and the force-field parameters are defined and kept fixed at the start of the MD simulation. Note that force-field parameters are defined for atom-types, that is atoms in the same chemi-

cal environment, such as amine-nitrogen, carbonyl-oxygen, etc. Prototyping is required to assign atom-type for each element in the polymer structure. The generation of bond topology and parameter setting is automated by separate software, moltemplate⁵⁾, in production computations.

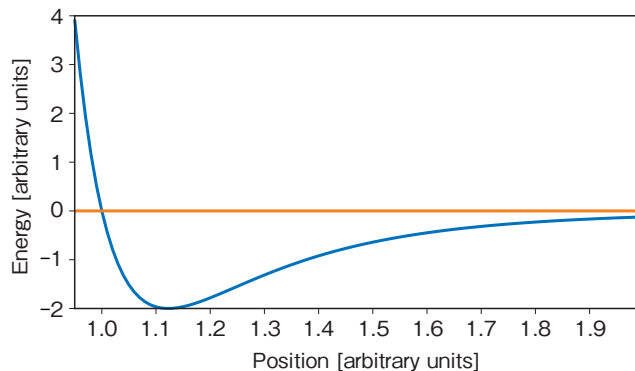


Figure 4 The Lennard-Jones 12-6 potential with the parameters $\epsilon = 2$ and $\sigma = 1$.

Bonding in metals is different from polymers and to describe the many-body effects in metallic systems a different functional form is typically required. Still, in our work we used a minimal Cu model, of pair-wise Lennard-Jones potential, which still reproduces the structural properties, lattice parameters and structural stability in solid state⁶⁾. The mixing of different classes of force-fields in the same simulation setup is not considered a good practice, so we aimed to use a unified potential with the same functional forms as already present in the polymer and metal models too.

Finally, the interaction model between the metal and polymer atoms is critical for quantitative results adhesion strength. We assumed that the adhesion is dominantly dispersive, and LJ 12-6 potential was used in the simulation model, neglecting any covalent bond formation processes. The interaction potential of chemically different materials is a challenging task and will be discussed later in more detail. For an overview of the approach for organic-inorganic interfaces see REFERENCES⁷⁾.

The initial geometry was generated in a complex process with different tools for the polymer and metal parts. The polyimide part consists of identical linear chains with typically $N=15$ repeat units of PMDA-ODA with a realistic bulk density of $\rho = 1.4 \frac{\text{g}}{\text{cm}^3}$. The entanglement of polymers corresponds to the theoretical prediction. The 3D periodic polymer geometries were generated by an energy-based Monte-Carlo method using EMC software⁸⁾. The chain length and the bulk density are input parameters to be set. For mixed, free and periodic, boundary condition, an MD annealing method was used by the heating and cooling of the model to relax the polymers to close to equilibrium configurations. The geometry of the copper substrate was generated as an ideal face-centered-cubic crystal, with the (111) surface orientation. Real surfaces have rough shape with various types of surfaces defects,

such as ledge, terrace, kink, or vacancy. We managed to incorporate such defects in the simulations, but the results were not systematically analyzed. The final step of the pre-processing was to merge the polymer and metal parts and run an MD simulation to equilibrate the system and ensure the realistic interface configuration.

In present simulation method external loading is applied to separate the interface and measure the adhesive strength. The first method is the displacement loading in which the metal substrate is fixed, and the polymer is moved by a constant displacement rate or velocity. Here the boundary condition is that a few atomic layers of Cu are fixed, and the upper part of the PI is moved as a rigid body. In case of static displacement loading, all Cu atoms are fixed, and all PI atoms are moved at a constant velocity. This is a rather poor approximation and can be used only as a reference to dynamical method. The second method is Steered Molecular Dynamics, SMD, technique⁹⁾, which was used in most production computations. In the SMD method the loading is not applied directly but by coupling to a fictitious mass point with a harmonic spring element connection. The advantage of this method over the first one is that both the loading force on the polymer and the free-energy change along the assumed reaction coordinate, Potential of Mean Force (PMF) are computed. We can use this energy, where the PMF approximates the equilibrium, thermodynamic work of adhesion.

Two configuration setups were used in the MD of adhesion, see Figure 5. In case of 2D slab setup, periodic boundary conditions are applied in horizontal directions and uniform loading is applied along the vertical direction on the top PI surface. In the 1D setup the system is periodic only in the normal direction to the figure, and free boundary conditions are used in the two other, horizontal and vertical directions. The loading is applied only to the small area at one of the ends of the polymer. This setup is reminiscent of the 90-degree peel test in experiments.

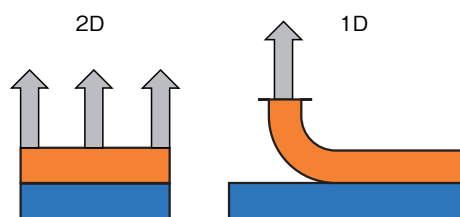


Figure 5 Illustration of the 2D, pulling, and the 1D, peeling setups.

DFT method is now established as the main electronic structure method in materials science research. We used DFT to compute the structure and energy of the polymer-metal slab system at a small length-scale containing up to 100 atoms and mainly for geometry optimization computations. The typical slab setup contains a Cu surface, with single molecules adsorbed on it. An example of DFT slab setup is shown in Figure 6.

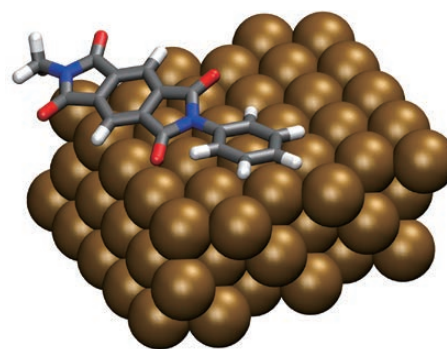


Figure 6 Adsorption setup of PI fragment on Cu (111) surface, optimized geometry obtained by slab DFT computations.

In technical details, the Generalized Gradient Approximation/Perdew-Burke-Ernzerhof (GGA/PBE) functional with D3 dispersion correction, Projector Augmented Wave (PAW), pseudo-potential, and plain-wave basis were used in Quantum-Espresso software¹⁰⁾. For fast pre-optimization in slab system semi-empirical quantum-mechanical method GFN1 were used in CP2K software. For single molecules properties such as atomic partial charges DFT computations with the General Atomic and Molecular Electronic Structure System (GAMESS)¹¹⁾, quantum-chemistry software was utilized.

3. RESULTS AND DISCUSSION

The simulation method presented previously was applied for adhesion computations. First, we discuss the results in the 2D setup. A slab setup had the size $L_x=15.3$ nm, $L_y=15.5$ nm, with number of PI chains $N_{chain}=73$ of length $N_{RU}=15$, totaling of $N_{PI}=40233$ atoms. In addition, the simulation cell contained $N_{Cu}=25200$ Cu atoms. We applied a constant temperature, volume and particle number simulation, at $T=300$ K. The SMD loading was applied with a spring constant $K=150 \frac{\text{kcal}}{\text{mol a}^2}$ and the loading speed was in the $v=0.1-100 \frac{\text{m}}{\text{s}}$ range. Compared to experiments, the simulation loading velocities are much overestimated but otherwise simulation time would be excessively long. We have used PI-Cu interaction parameters uniform $\epsilon_{PI-Cu}=0.1 \frac{\text{kcal}}{\text{mol}}$ and $\sigma_{PI-Cu}=0.28$ nm. Representative result of $v=0.1 \frac{\text{m}}{\text{s}}$ is presented in Figure 7. The separation of PI and Cu is not uniform, some polymer chains are already detached but other parts are still in contact with the metal substrate, even when the top part of the polymer is moved with up to $\Delta d=2.0$ nm.

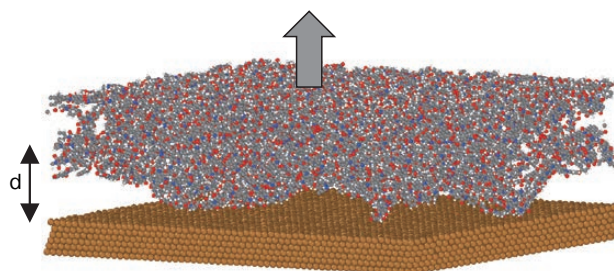


Figure 7 Snapshot of an intermediate Copper substrate.

The results for energy change, and force on PI surface are shown in Figure 8. The required force to move the PI part increases initially, reaching a maximum value, then a gradual decrease was measured. The energy curve is measured from simulation, but alternatively it could be derived from integrating the force to obtain the energy of adhesion.

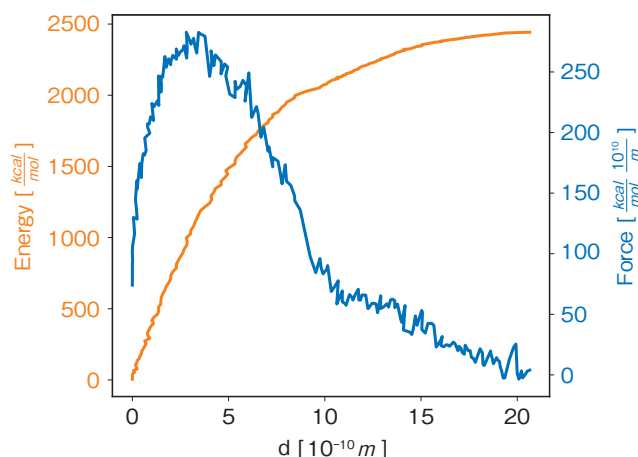


Figure 8 The force and energy as function of displacement in dynamic loading.

We investigated the effect of loading speed on the measured energy of adhesion. The result is shown in Figure 9. As the loading speed decreases the numerical values converge to the quasi-static limit energy value, which corresponds to the energy of adhesion. In this setup the loading speed $v = 1 \frac{\text{m}}{\text{s}}$ can be considered good enough for quantitative results. The possible explanation of this effect is that the energy of external loading is converted to break the interface bonds and mechanical deformation of the PI material. At large loading velocities this energy term is comparable to the energy for creating the two free surfaces. Choosing an optimal loading speed parameter is critical because the simulation time is inversely proportional to the loading velocity.

We changed other parameters such as the horizontal size, the thickness of the PI film and the number of monomers in PI chains. We observed no significant changes in the energy and force results. We considered the minimal physically sensible system size when the vertical and horizontal directions exceeded the radius of gyration of PI.

An interesting question is, when the loading in 2D system is applied not vertically but in a horizontal direction, as a shear deformation setup. We observed that in the case of a sliding deformation, both the force and energy values are very small, as the interface has negligible shear adhesion strength, and two substrates move along without much resistance. The result is not surprising because the Lennard-Jones potential cannot describe shear strength.

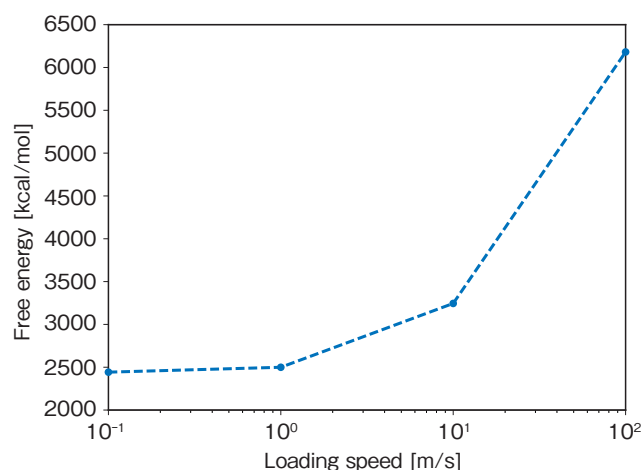


Figure 9 The dependence of the measured adhesion energy as a function of loading velocity, for selected points. The line is the guide to the eye.

The second setup was the 1D periodic slab system with loading like the experimental peel test setup in Figure 10. The size of the simulation cell was chosen to be $L_x = 30.6 \text{ nm}$, $L_y = 5.7 \text{ nm}$ and the polymer thickness is about $L_z = 3.5 \text{ nm}$ initially. The total number of atoms was $N = 49366$. Loading was applied for $\Delta L_x = 2 \text{ nm}$ section of the PI. Loading speed was set $v = 1 \frac{\text{m}}{\text{s}}$ and $v = 10 \frac{\text{m}}{\text{s}}$. The force-field parameters were the same as in the 2D setup.

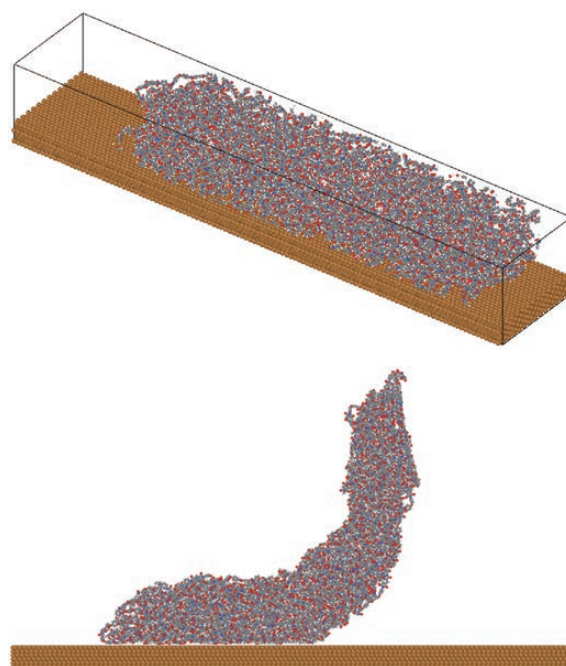


Figure 10 The initial position (upper figure) and intermediate position (lower figure) in the 1D setup.

The loading process in the 1D model starts with an initial stage when the polymer around the loading point is detached from the metal substrate and the crack tip is formed. Then in the second stage a constant velocity crack propagation is observed along the metal substrate. The final stage takes place when the complete separation of polymer and metal parts is achieved. The force and

energy functions in the peeling process are shown in Figure 11. The maximum force is observed at the initial stage during which the crack tip is formed. In the second stage the force required for a crack propagation drops significantly. This can be related to bonds broken per unit time at the crack tip. Although the force data is rather noisy, an average force value can be derived. The noise level for the energy function is much smaller because it is computed as the integral of the force. After the transient stage energy follows a linear trend.

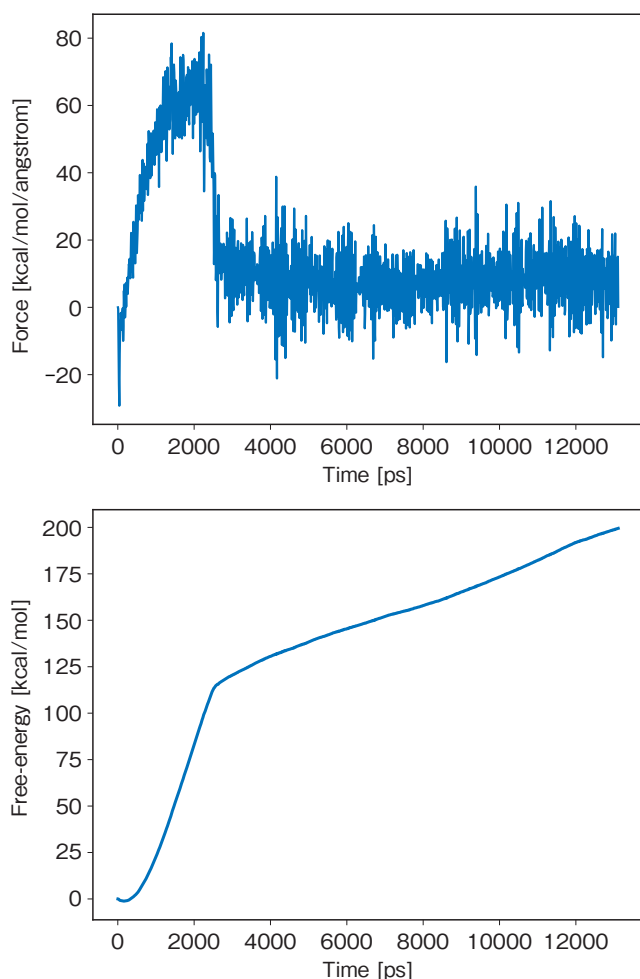


Figure 11 The force (upper figure) and the energy (lower figure) as function of time in the 1D setup.

The adhesion strength from the 2D and 1D simulation results is derived from the force and energy data. In the case of the 2D model, it is the energy per surface area $f = \frac{E}{A}$, and in the 1D model the average loading force per width of the simulation cell, $f = F/L_y$. Computed values are consistent, but they are in the range of $f = 0.07 - 0.09$ N/m which is very low compared to experiment measurements.

The polymer-metal interaction model determines the quantitative predictions of the simulation model. Unfortunately, accurate force-field parameters are not directly available, and we had to use an order of magnitude estimate, considering that polymer-metal interaction is weaker than the internal cohesion in PI. The fitting of

force-field parameters is demonstrated for the slab setup of adsorption configuration shown in Figure 12. Single point energies were computed for a static scan as the PI fragment was moved in a vertical direction as a rigid object. The geometry of the configurations with respective relative energies were prepared as input for the potential fitting program, atomicrex¹²⁾. Assuming LJ 12-6 interaction of polymer with metal atoms, the parameter fitting is performed.

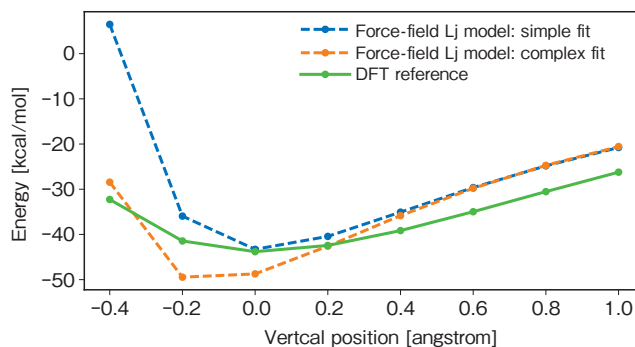


Figure 12 Comparison of the relative energies of DFT and two force-field parameterizations for the PI fragment rigid scan on Cu surface. Lines are the guide to the eye.

We obtained value of $\epsilon = 0.3 - 0.4 \frac{\text{kcal}}{\text{mol}}$ depending on the weighting method, which is larger but of the same order of magnitude as used previously in Figure 11. The fitted distance parameter was the same $\sigma = 0.28$ nm as previously. The fitting method is simplified because of the limited data used and that the functional form of the fitted potential is very simple. Training data set can be generated from DFT MD trajectories or using different adsorbents.

4. SUMMARY AND OUTLOOK

We have developed a computer simulation framework to investigate adhesion of the polyimide-copper interface by using atomistic Molecular Dynamics simulations. DFT computations on small systems were used for validation and to improve force-field model parameterization. The strength of our method is the meticulous model system preparation and the integration of several separate computational tools, resulting in highly customizable software. The simulation model can describe realistic polymer structure, mechanical loading processes with atomistic details that are not accessible to experimental methods. Various parameters on adhesion strength can be studied such as surface defects and surface roughness, presence of additives, temperature effects, to name a few. While the inter-atomic potentials for the polymer and copper have been validated, the interface potentials were rather oversimplified. We demonstrated how DFT computed data can be used for parameters fitting. Our method is capable of comparative peel force analysis but computing an estimation of absolute peel force is beyond the scope of this model. The limitation of the model is that

large scale physics, anchor effects and stiffness of the real thickness film are not taken into account.

The simulation method presented here can be modified to describe other polymers and extended to metal-oxide substrates with ionic character or ceramics. When chemical bond formation is important in the adhesion process, reactive types of potentials need to be used. An alternative could be the recent machine learning (ML) potentials, which have a general functional form, that can be trained on a large set of reference configurations. Recently pre-trained potentials of ML force-fields have become available¹³⁾, which will have an impact on the force-fields selection in materials simulations.

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